

SUPPRESSION OF BaF₂ SLOW COMPONENT OF X-RAY LUMINESCENCE IN NON-STOICHIOMETRIC Ba_{0.9}R_{0.1}F_{2.1} CRYSTALS (R=RARE EARTH ELEMENT)

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ABSTRACT

A series of BaF₂ crystals doped with 10% mole fraction of each rare earth element has been grown, and the effect of these dopants on the slow luminescence (due to anionic self trapped excitons) and fast luminescence (due to core-valence transitions) has been studied. While significant suppression was observed for both components, the best dopants for suppressing the slow component of barium fluoride (up to 25–50%) while maintaining the luminosity of the fast component are La, Y, and Lu. The luminescence of Ba_{0.9}Eu_{0.1}F_{2.1} is almost entirely fast (>90%), but with low light output. For two rare earth dopants (La and Gd), the effect of slow and fast component suppression was studied as a function of concentration (Ba_{1-x}R_xF_{2+x} with x = 0.5 for R=La and x = 0.3 for R=Gd). The suppression is non-linear with dopant concentration, with the relative degree of slow component suppression correlated with the melting point of these samples.

INTRODUCTION

Barium fluoride plays a major role in the new generation of fast (nanosecond) scintillators, because the very fast core-valence electron transition (or cross-luminescence) in it is most vividly manifested [1,2]. However, fast BaF₂ core-valence transitions (CVT) (800 ps and 220 nm) are combined with a more intense slow component (600 ns and 300 nm) that hinders the count rate capability of these crystals when used as fast scintillators. In addition, the strong temperature dependence of this slow component deteriorates the stability of emitted light intensity.

The slow component is due to relaxation of self trapped anionic excitons (STE). Such defects are typical of ionic fluorides, but are stable and luminous at ambient temperature only in fluorides with CaF₂ structural type. Therefore, studies of luminescence of STE are also of general interest with regard to fluoride scintillators with fluorite type structure. These phases comprise a large family of multicomponent non-stoichiometric crystals [3,4] containing some dense and radiation hard materials [5]. In these M_{1-x}R_xF_{2+x} phases [6] the suppression of the intrinsic slow component has been qualitatively observed in CaF₂, SrF₂, and BaF₂ crystals with R = rare earth at x = 0.1–0.3 (*i.e.* 10–30 mole % RF₃), and this effect has been studied in more detail for Ba_{1-x}R_xF_{2+x} [7–11]. Dopants also affect other characteristics of BaF₂, such as the mechanical hardness, ease of cleavage [3], and density. For example, Ba_{0.69}La_{0.31}F_{2.31} has a mechanical hardness of 250 kg/mm² compared to 80 kg/mm² for BaF₂. While BaF₂ has a density of 4.89 g/cm³, Ba_{0.85}Gd_{0.15}F_{2.15} has a density of 5.28 g/cm³ and the density of Ba_{1-x}U_xF_{2+x} can exceed 7 g/cm³ [5].

Despite the great number of works dedicated to improving the luminescent characteristics of BaF₂ by enhancing the absolute and/or relative intensity and decay time of the fast component, the effect of various RF₃ dopants on its spectroscopic characteristics is still unclear. There are large variations in the selected dopant concentration, differences in crystal growth method, as well as unexplained sample to sample differences of luminescent characteristics.

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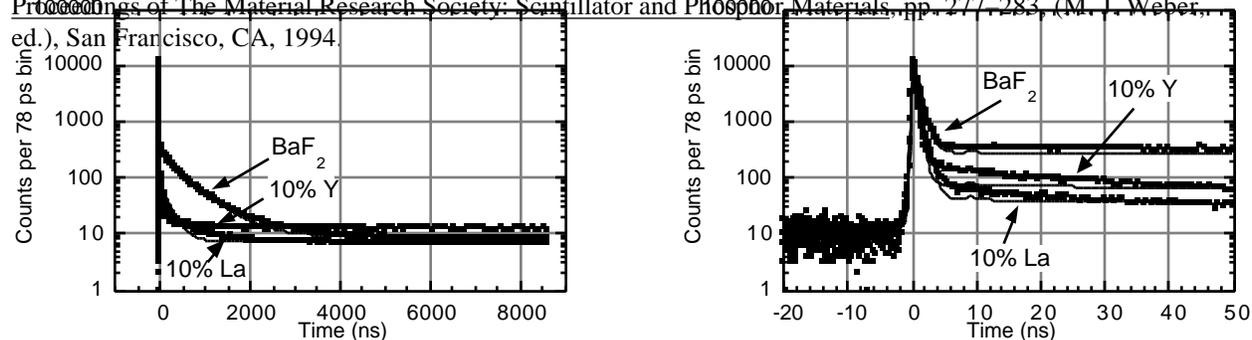


Figure 1: Raw decay time data collected for three samples (BaF_2 , $\text{Ba}_{0.9}\text{La}_{0.1}\text{F}_{2.1}$, and $\text{Ba}_{0.9}\text{Y}_{0.1}\text{F}_{2.1}$). The curve on the left shows the full time range, the curve on the right shows an expanded view of small times.

Therefore, we have performed a systematic study X-ray luminescence of $\text{Ba}_{1-x}\text{R}_x\text{F}_{2+x}$ with a nominal mole fraction (x) of 10% and $R = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu},$ and Y . These crystal compositions were grown by Bridgeman-Stockbarger technique in a fluorinating atmosphere [12,13]. The chemical composition of most crystals was verified by measurements of unit cell parameters and did not differ significantly from nominal values.

MEASUREMENT METHOD

Scintillation decay time spectra were measured with the delayed coincidence method [3,4]. Powdered samples were placed in quartz cuvettes (5 mm outer diameter, 0.3 mm wall thickness) and irradiated with a brief X-ray pulses. The fluorescent emissions were detected with a sapphire windowed microchannel plate photomultiplier tube [15]. A time to digital converter digitized the time between the X-ray pulse and the detected scintillation photons in 78 ps bins, and data were collected for 7500 seconds for each sample. The instrumental response (*i.e.* the X-ray pulse width convolved with the response of the time measurement system) was measured to be 410 ps fwhm.

The scintillation decay time spectra for three samples (BaF_2 , $\text{Ba}_{0.9}\text{La}_{0.1}\text{F}_{2.1}$, and $\text{Ba}_{0.9}\text{Y}_{0.1}\text{F}_{2.1}$) are shown in Fig. 1. The spectra are fit to the sum of two exponential decay components plus a flat background, and the resulting fits also shown in Fig. 1. While more than two decay components are needed to accurately model the observed spectra, the purpose of this work is to identify crudely the relative amounts of fast and slow scintillation light, and so the fit is limited to two components. From these fits, the decay lifetimes of the fast and slow components are extracted, as well as the number of photons in each of these components and the background. For BaF_2 , decay times of 0.73 ns and 560 ns are obtained for the fast and slow components, and 1.77×10^5 , 1.91×10^6 , and 1.127×10^6 counts are observed in the fast, slow, and background components respectively.

Variations in light collection efficiency due to optical attenuation length differences make accurate light output measurements from powdered samples impossible. An estimate of the relative scintillation efficiency can be made by assuming that all samples have the same optical attenuation length, and so directly comparing the observed number of photons. The absolute scintillation efficiency can be crudely estimated by normalizing to the accepted luminosity for BaF_2 (fast component = 1800 photons/MeV, slow component = 8000 photons/MeV [16]). Separate normalization factors are required for the two components, as the sapphire windowed photomultiplier tube has different quantum efficiencies for the fast light ($\lambda = 220$ nm) and the slow light ($\lambda = 300$ nm).

An estimate of the amount of DC light with decay time longer than the 10 ms X-ray excitation rate is made by subtracting from the fit value of the background a contribution from dark current (8×10^5 counts) to obtain the number of counts due to DC light. This is converted to absolute light output using the slow light conversion factor. Unfortunately, this measure has large errors due to the non-statistical fluctuations in the dark current in the microchannel plate photomultiplier tube. All

samples are analyzed using this method, and the results shown in Table 1 and the luminosities of the fast and slow components shown as a scatter plot in Fig. 2.

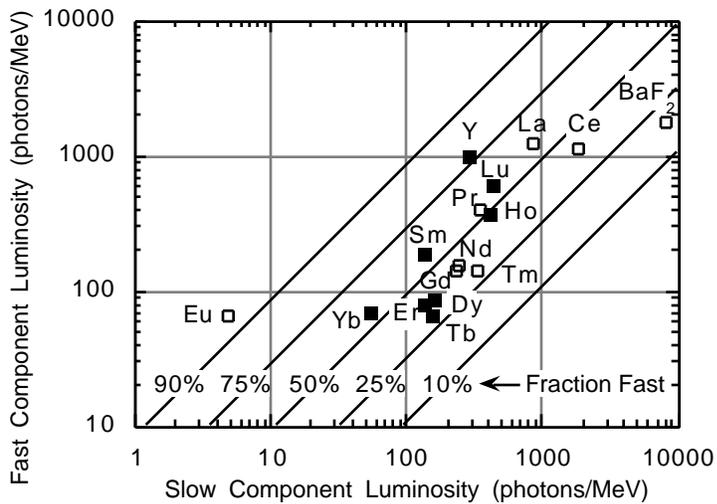


Figure 2: Comparison of the absolute luminosity of the fast and slow components of $Ba_{0.9}R_{0.1}F_{2.1}$. Open squares denote dopant elements studied in [8], solid squares are additional elements studied in this work.

Material	Fast Component Luminosity (photons/MeV)	Fast Component Decay Time (ns)	Slow Component Luminosity (photons/MeV)	Slow Component Decay Time (ns)	DC Component Luminosity (photons/MeV)
Ba F ₂	1805	0.73	7997	559	1364
Ba _{0.9} La _{0.1} F _{2.1}	1258	0.41	856	205	-4
Ba _{0.9} Ce _{0.1} F _{2.1}	1149	7.29	1862	39	-346
Ba _{0.9} Y _{0.1} F _{2.1}	1000	0.72	289	167	2445
Ba _{0.9} Lu _{0.1} F _{2.1}	594	0.43	430	175	8
Ba _{0.9} Pr _{0.1} F _{2.1}	407	2.19	356	175	212
Ba _{0.92} Ho _{0.08} F _{2.08}	367	0.27	416	148	-179
Ba _{0.9} Sm _{0.1} F _{2.1}	186	0.22	138	121	-445
Ba _{0.9} Nd _{0.1} F _{2.1}	155	0.32	246	120	-178
Ba _{0.9} Tm _{0.1} F _{2.1}	140	0.34	328	201	-80
Ba _{0.9} Gd _{0.1} F _{2.1}	140	0.26	234	130	5629
Ba _{0.9} Dy _{0.1} F _{2.1}	85	0.17	165	126	-484
Ba _{0.9} Er _{0.1} F _{2.1}	79	0.20	136	95	-245
Ba _{0.9} Yb _{0.1} F _{2.1}	69	0.23	54	84	1971
Ba _{0.9} Tb _{0.1} F _{2.1}	67	10.79	153	201	3514
Ba _{0.9} Eu _{0.1} F _{2.1}	66	0.17	5	14	3668
Ba _{0.995} La _{0.005} F _{2.005}	1113	0.78	2240	480	475
Ba _{0.9} La _{0.1} F _{2.1}	1258	0.41	856	205	-4
Ba _{0.85} La _{0.15} F _{2.15}	298	0.61	39	75	228
Ba _{0.75} La _{0.25} F _{2.25}	328	0.61	29	69	-211
Ba _{0.675} La _{0.325} F _{2.325}	392	0.68	32	51	6
Ba _{0.5} La _{0.5} F _{2.5}	622	0.69	1499	385	3375
Ba _{0.999} Gd _{0.001} F _{2.001}	1189	0.82	3221	518	2131
Ba _{0.99} Gd _{0.01} F _{2.01}	758	0.68	1245	363	2908
Ba _{0.97} Gd _{0.03} F _{2.03}	578	0.55	848	258	4906
Ba _{0.95} Gd _{0.05} F _{2.05}	363	0.43	493	211	4432
Ba _{0.91} Gd _{0.09} F _{2.09}	438	0.26	582	155	10563
Ba _{0.9} Gd _{0.1} F _{2.1}	140	0.26	234	130	5629
Ba _{0.8} Gd _{0.2} F _{2.2}	29	0.31	73	62	3775
Ba _{0.7} Gd _{0.3} F _{2.3}	14	0.68	29	38	2409

RESULTS

Accurate timing is impossible unless the luminosity of the fast component is large. Therefore, the most interesting samples are those with more than half of the fast component luminosity of BaF₂. Only three dopants (La, Ce, and Y) meet this 900 photons/MeV criteria. For the sample with Ce, the intrinsic barium fluoride luminescence has been replaced by Ce³⁺ 4f-5d luminescence having 7.3 and 39 ns decay time components [17] and thus is not relevant to this work. Similar effects were observed with Pr (2.2 ns) and Tb (11 ns), and while the emission spectra were not measured, these emissions are not due to BaF₂ CVT.

With the exception of those previously mentioned compounds whose fast CVT luminescence is replaced by another mechanism, the decay time of the fast BaF₂ component (0.73 ns for crystals grown in fluorinating atmosphere) was decreased by the addition of the dopant. This decrease was smallest for $R = Y$ (0.72 ns), Lu (0.43 ns), and La (0.41 ns), while for $R = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm,$ and Yb the decay times lie in the interval 0.32 – 0.17 ns. The decay times of the slow component are also reduced for these compounds, ranging from 205 ns (La) to 84 ns (Tb).

For the Eu doped sample, the barium fluoride anionic STE emission appears to be replaced by another weak emission with a relatively short (14.1 ns) decay time. Table 1 shows that some samples, including undoped BaF₂ and solid solutions with $R = \text{Eu, Gd, Tb, Yb, and Y}$, may have an additional very long ($\gg 10$ ms) decay component.

The effect of RF_3 concentration on slow component suppression was also studied for two series of solid solutions, Ba_{1-x}La_xF_{2+x} ($x = 0.5$) and Ba_{1-x}Gd_xF_{2+x} ($x = 0.3$), and the results from these samples also included in Table 1. For both dopants, the relative fast component intensity (% of total light output due to the fast emissions) pass through maxima as the RF_3 content increases. The absolute intensities of the fast and slow components for the Ba_{1-x}La_xF_{2+x} series are shown as solid squares in Fig. 3, along with similar data from [8] shown as open squares. While each data set is reasonably self-consistent, there is quantitative disagreement between the two data sets, possibly due to the difference in crystal growth conditions.

DISCUSSION

The suppression of the slow (STE) component of BaF₂ is common to all rare earth ions. While accurate quantitative studies of this effect require corrections for possible absorption of the STE emissions by R^{3+} ions, qualitative observation shows that most R^{3+} dopants (at 10 mole %) produce a similar effect. In Fig. 2 one can see that the fraction of fast component intensity for most R^{3+} is near to 25 – 50 %. The best dopants for suppressing the slow component of barium fluoride without quenching the fast component are La, Y, and Lu. All these ions have filled electronic shells. The fast component of Ba_{0.9}Y_{0.1}F_{2.1} is reduced by a factor of less than two, but the slow component is reduced by a factor of nearly 30. For Ba_{0.9}Lu_{0.1}F_{2.1} the fast component of is reduced by a factor of three and the slow component is reduced by nearly 20.

The compound with the largest fraction of fast component is Ba_{0.9}Eu_{0.1}F_{2.1}, which has >90% of its emissions in the fast component, albeit a very small total light output. It is possible that a lower dopant concentration could yield a material with higher total light output and nearly total suppression of the slow decay component.

The 10% RF_3 fraction selected for these crystals is not necessarily optimal for slow component suppression, so further studies are necessary to study the dependence on RF_3 concentration in solid solutions. Preliminary studies of this kind were made for two dopants: La and Gd. It is interesting to note that while the maxima of the fraction of the total luminosity in the fast component versus concentration are different for the two samples (near 30 mole % for LaF₃ and near 9% for

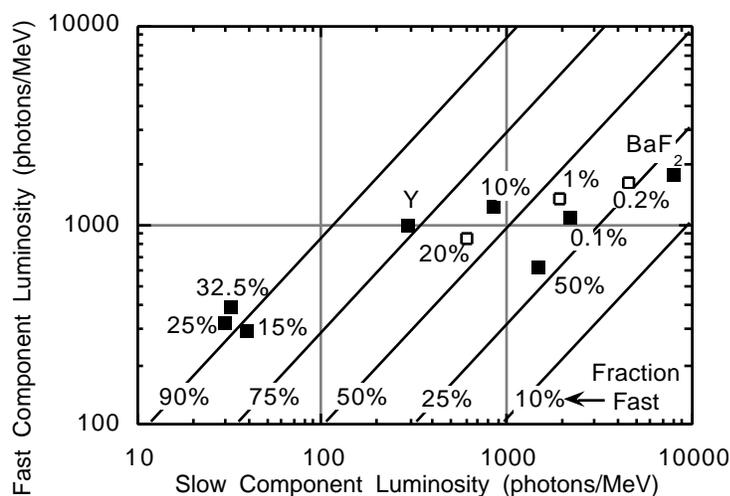


Figure 3: Comparison of the absolute luminosity of the fast and slow components of Ba_{1-x}La_xF_{2+x}. The solid squares data from this work, the open squares denote data from [8].

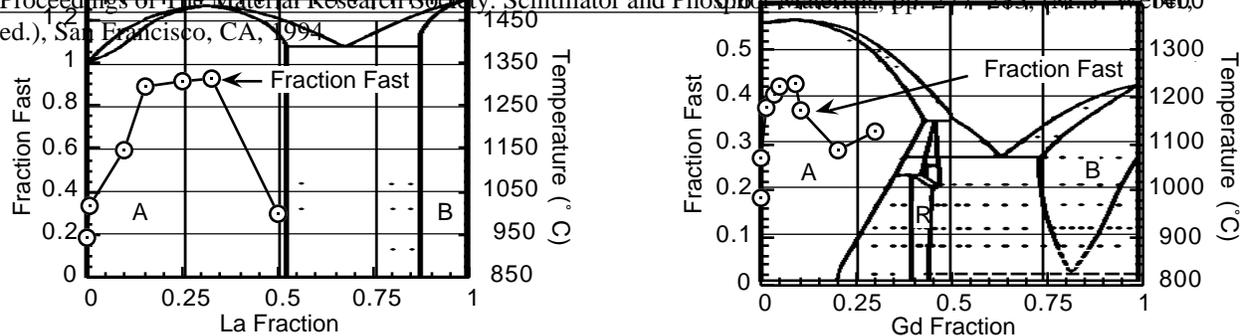


Figure 4: Fraction of the total luminosity in the fast component versus concentration superimposed on the phase diagram (*i.e.* melting point vs. concentration) for Ba_{1-x}La_xF_{2+x}, and Ba_{1-x}Gd_xF_{2+x}.

GdF₃ – see Fig. 4), the positions of these maxima are close to the maxima on the melting curves of corresponding solid solutions [18]. This observation is very important for the growth of multicomponent materials because of the pseudo single-component (congruent) melting of these compositions. The anomaly of the melting of heterovalent solid solutions is the direct consequence of strong chemical interactions in non-stoichiometric Ba_{1-x}R_xF_{2+x} crystals accompanied by the formation of clusters of structural defects.

It is conceivable that the mechanism of slow and fast BaF₂-component suppression by R³⁺ is closely related to crystal structure features of non-stoichiometric Ba_{1-x}R_xF_{2+x} crystals. Interstitial anions and anionic vacancies accompany this type of heterovalent isomorphism with a variable number of atoms in the unit cell. The types of crystallographic positions of interstitial fluorine and their occupancies change with total concentration of RF₃ in Ba_{1-x}R_xF_{2+x} solid solutions, as well as cation – anion distances and coordination numbers of constituent ions. To test this hypothesis, we looked for correlations between CVT and STE suppression and the geometric parameters of solid solutions (mean ionic radii or unit cell parameters), but do not observe any such correlations.

Some common structural features of CaF₂-type structure and non-stoichiometric Ba_{1-x}R_xF_{2+x} phases may also affect slow and fast component suppression. Cations in non-defect CaF₂ type structure have a cubic surrounding of fluorine ions with metal – fluorine distance equal to the sum of ionic radii. The study of defect crystal structure of grossly non-stoichiometric Ba_{1-x}R_xF_{2+x} phases [19] shows the formation of some (*M*, *R*) – F distances that are 12% shorter than characteristic ones. This reduction is typical of BaF₂ based phases and refers to F-ions in the 48-fold *i*-complex of space group *Fm3m*, which are displaced from the centers of large cubic voids along the 2-fold axis. Proceeding only from structure data, we can not decide to what extent this reduction is attributed to Ba – (*i*-F) or R – (*i*-F) distances. We assume that an increase of the coordination number (c.n.) of large Ba-cations is more probable than that of a smaller R-cations. Thus, there are two factors at least (reduction of some cation – anion distances and an increase of barium c.n.), which can be responsible for the observed influence of R³⁺ on CVT fast luminescence in Ba_{1-x}R_xF_{2+x} crystals.

Intrinsic slow luminescence of BaF₂ is due to relaxation of anionic self trapped excitons, which is related to quasi-molecular excited (F₂⁼)^{*} formation [20] with the axes of these fluorine pairs directed along the 2-fold axis. The results of [19] agree with this assumption, that is, with interstitial F-ions in the *i*-position of the *Fm3m* space group. The anionic defects introduced by irradiation are metastable. Some of the interstitial fluorine-ions in Ba_{1-x}R_xF_{2+x} solid solutions occupy the same crystallographic positions, which are occupied by F¹⁻ in BaF₂ during formation of anion excitonic pairs (F₂⁼)^{*}. The position of interstitial F-ions is equal for all R in the Ba_{0.9}R_{0.1}F_{2.1} crystal structure, but can vary with RF₃ concentration. Those defects in solid solutions are “chemically introduced” and are stable at low and high temperatures (up to 1000°–1500° C). Apparently, partial occupation of large voids (F-cubes) in CaF₂ type structure by stable defects affects the formation and behavior of metastable (F₂⁼)^{*} quasi-molecules created by X-ray irradiation.

CONCLUSION

The suppression of the slow and fast components of BaF_2 luminescence was measured in samples of $\text{Ba}_{0.9}\text{R}_{0.1}\text{F}_{2.1}$ crystals with R = all rare earth elements. While the absolute luminosity of the fast component varies over two orders of magnitude for different R , the fraction of fast component luminosity lies between 25% and 50% for most rare earth elements. The best dopants for slow component suppression were La, Y, and Lu. Addition of these dopants effects more than the slow component suppression, and can also be used to improve other (mechanical, radiation hardness, density) characteristics of multicomponent BaF_2 -based fast scintillators. The dependence of the suppression on RF_3 concentration is studied in $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ ($x = 0.5$) and $\text{Ba}_{1-x}\text{Gd}_x\text{F}_{2+x}$ ($x = 0.3$) crystals. It is important for crystal growth that the maxima of slow component suppression are close to the maxima on the melting curves of these solid solutions.

Only a small part of the fluorite family of non-stoichiometric phases $M_{1-x}\text{R}_x\text{F}_{2+x}$ ($M = \text{Ca, Sr, Ba, Cd, Pb, Hg}$ and $R = \text{rare earth elements, Al, Ga, In, Tl}^{3+}, \text{Bi}$, and some other 3+ and 2+ cations) have been studied. The search for the best dopants should be continued with other chemical elements and different concentrations. The data on mechanisms of formation and spectroscopic behavior of anionic excitons in $M_{1-x}\text{R}_x\text{F}_{2+x}$ crystals should be compared with data on defect crystal structure of appropriate non-stoichiometric phases. Some multicomponent fluoride materials (two-component crystals are the simplest ones) with CaF_2 type structure have rather high densities and good radiation hardness, and so are potentially interesting as heavy and fast scintillators.

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REFERENCES

- [1] N.N. Ershov, N.G. Zacharov, et al., *Optika i Spektroskopia* **53**, 89 (1982) (in Russian).
- [2] M. Laval, M. Moszynskii, et al., *Nucl. Instrum. Meth.* **206**, 169 (1983).
- [3] B.P. Sobolev, *Butll. Soc. Cat. Cien.* **12**, 275 (1991).
- [4] B.P. Sobolev and P.P. Fedorov, *Inorganic Chemistry* **29**, 382 (1993).
- [5] V.G. Vasilchenko, M. Kobayashi, Ch. 3, 6 in: *Multicomponent Crystals based on Heavy Metal Fluorides for Radiation Detectors*, edited by B.P. Sobolev and E. Casassas (Institute d'Estudis Catalans, Barcelona, Spain, 1994, in press).
- [6] Sh. Vachidov, G.A. Tavshunskii, et al., *Zhurnal Techn. Fiziki* **49**, 1943 (1979) (in Russian).
- [7] P. Schotanus, C.W.E. van Eijk, et al., *IEEE Trans. Nucl. Sci.* **NS-34**, 272 (1987).
- [8] C.L. Woody, P.W. Levy, J.A. Kierstead, *IEEE Trans. Nucl. Sci.* **NS-36**, 536 (1989).
- [9] P.A. Rodnyi, M.A. Terechin, et al., *Spectra and Model of Luminescence of Barium-based Fluorides*, edited by *Inst. of Atomic Energy*, IAE - 4963/11, Moscow 1989, p. 15.
- [10] A.V. Golovin, E.N. Melchakov et al., *Fizika Tverdogo Tela* **31**, 253 (1989) (in Russian).
- [11] E.N. Melchakov, P.A. Rodnyi, et al., *Optika I Spektroskopia* **69**, 1069 (1990) (in Russian).

Proceedings of The Material Research Society: Scintillator and Phosphor Materials, pp. 277–283, (M. J. Weber, ed.), San Francisco, CA, 1994.

- [12] B.P. Sobolev, Z.I. Zhmurova, et al., in: *Growth of Crystals*, v.16, edited by Consultants Bureau, NY and London, 1988, p. 65.
- [13] P.P. Fedorov, T.M. Turkina, B.P. Sobolev, *Butll. Soc. Cat. Cien.* **13**, 258 (1992).
- [14] L.M. Bollinger and G.E. Thomas, *Rev. Sci. Instr.* **32**, 1044 (1961).
- [15] S.C. Blankespoor, S.E. Derenzo, W.W. Moses, et al., *IEEE Trans. Nucl. Sci.* **NS-41** (accepted for publication), (1994).
- [16] P. Dorenbos, J.T.M. de Haas, et al., *IEEE Trans. Nucl. Sci.* **NS-38**, 178 (1991).
- [17] W.W. Moses, S.E. Derenzo, *IEEE Trans. Nucl. Sci.* **NS-36**, 173 (1989).
- [18] B.P. Sobolev, N.L. Tkachenko, *J. Less-Common Metals* **85**, 155 (1982).
- [19] V.B. Alexandrov, *Butll. Soc. Cat. Cien.* **12**, 333 (1991).
- [20] M.N. Kabler, D.A. Patterson, *Phys. Rev. Lett.* **19**, 652 (1967).